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PHASE COMPOSITION AND STRUCTURE OF ALUMINUM – COATING COMPOSITE

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Low-melting enamel coatings for household aluminum kitchenware are synthesized. The possibility of formation of low-melting glasses in the system $R_2O – Al_2O_3 – B_2O_3 – TiO_2 – P_2O_5$ is studied. An optimum glass matrix composition with a decreased firing temperature (580°C) is selected.

The quality and properties of glass-enamel coatings to a large extent are predetermined by the phase composition and structure of the coating itself, by the type of interaction between aluminum and the coating, and by the composition of the adhesive layer.

In developing compositions and technologies for depositing tinted enamel coating on aluminum kitchenware, we took the aluminoborophosphate system as the basis for subsequent modifications [1].

To investigate the properties and structure of the metal – coating composite, we developed an optimum glass matrix composition ensuring the production of a high-quality low-melting enamel coating for aluminum in the system $R_2O – RO – B_2O_3 – Al_2O_3 – TiO_2 – P_2O_5$ [RO) CaO + ZnO; R_2O) $Li_2O + K_2O + Na_2O$].

To develop a glass matrix ensuring the production of a coating for aluminum with increased adhesive strength and chemical resistance, modeling of chemical compositions was performed in order to identify the optimum one. Based on preliminary studies, the ratio $Al_2O_3 : P_2O_5$ was taken equal to 0.75 – 1.00 with 11.25 – 16.25% B_2O_3 content (Table 1) [2].

Based on the proposed glass matrices, the following enamel slips were prepared (wt.%): 100 frit; above 100%:

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TABLE 1

Glass matrix	Mass content, %									
	P_2O_5	Al_2O_3	B_2O_3	TiO_2	K_2O	Li_2O	Na_2O	CuO	BaO	ZnO
1	30.75	23.00	11.25	8.50	11.00	–	16.50		–	4.00
2	30.80	29.20	10.00	10.00	–	–	10.00	–	–	10.00
3	34.00	30.00	11.00	9.00	–	4.00	12.00	–	–	–
4	25.96	17.15	42.97	–	–	2.20	11.76	–	–	–
5	51.12	27.71	7.86	–	1.00	1.00	12.13	–	–	–
6	32.00	30.00	8.00	5.00	–	–	14.00	–	5.00	6.00
7	32.78	24.82	11.25	6.50	1.50	2.00	21.15	–	–	–
8	69.54	6.93	2.07	–	–	1.14	–	9.52	–	10.84
9	44.00	21.20	7.10	–	–	3.70	20.00	4.00	–	–
10	48.20	21.70	–	2.40	9.20	–	18.50	–	–	–
11	68.45	2.78	1.91	–	–	1.91	–	15.37		9.58
12	72.25	2.24	1.54	–	–	1.32	–	12.00		10.06
13	38.00	24.00	7.00	9.00	2.00	–	20.00	–	–	–
14	33.00	23.00	11.00	7.00	1.00	4.00	21.00	–	–	–
15	24.00	22.00	12.00	–	–	–	7.20	9.00	9.00	15.80
16	30.00	27.00	10.00	10.00	–	8.04	18.05	–	–	6.91
17	32.00	25.00	10.00	9.00	–	–	5.00	4.00	9.00	6.00
18	32.00	25.00	8.00	7.00	–	–	12.50	5.00	5.00	5.50
19	32.00	25.00	9.00	7.00	–	4.00	12.50	–	5.25	5.25
20	32.00	25.00	8.00	9.00	3.50	–	15.00	2.50	–	5.00
21	32.00	29.00	8.00	–	4.00	4.00	20.00	–	3.00	–
22	32.00	29.00	–	–	4.00	4.00	20.00	4.00	–	9.00

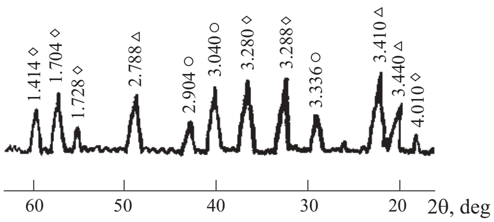

Fig. 1. The diffraction pattern of a coating with a transitional layer: ○) $Na_2O \cdot P_2O_5$; △) $Al_2O_3 \cdot P_2O_5$; ◇) $Al_2O_3 \cdot Cr_2O_3$.

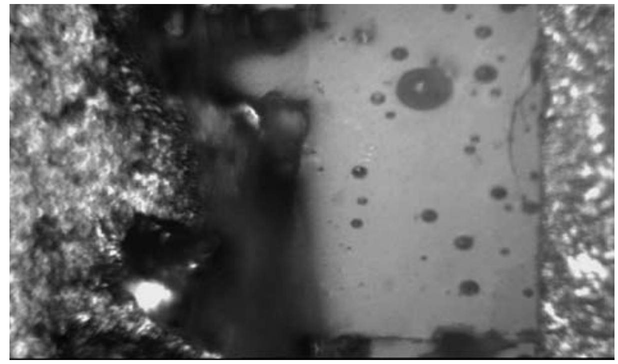

Fig. 2. Electron microscope photo of a coating with a transitional layer.

0.5 clay, 0.5 $NaNO_2$, and 40.0 water. The optimum glass matrix composition was chosen based on its significant properties, i.e., adhesion in the aluminum-coating system and chemical resistance.

It was found that composition 7 has the best adhesion strength and chemical resistance. Its strength of adhesion to aluminum is 72%, it has high resistance to aqueous and alkaline media with a weight loss in boiling equal to 0.019%. Furthermore, this composition has high chemical resistance to class A acids, luster (mirror reflection coefficient) equal to 41%, thermal resistance over 50 thermal cycles, and impact strength satisfying the requirements of GOST 15140–78, GOST 9.302–88, and GOST 24788–81.

The metal before enamel application was treated according to the following schedule:

– composition 50 g/liter Na_2CO_3 and 50 g/liter Na_3PO_4: treatment temperature 85 – 90°C, duration 5 min, washing with hot water;

– composition 50 g/liter Na_2CO_3, 25 g/liter K_2CrO_4, and 20 g/liter NaOH: treatment temperature 60 – 70°C, duration 15 – 20 min; annealing at 500°C for 5 min.

To obtain data on the phase composition of the coating, its x-ray phase analysis was performed. The diffraction patterns were recorded directly from the surface of the coating; moreover, x-ray analysis was made layer by layer in consecutive polishing of the coating.

The type, phase composition, and mutual arrangement of phases in a coating and in the transitional layer are the determining factors in producing aluminum – coating composites with certain service properties. While the structure of coatings for steel and copper underwent comprehensive analysis and research, the structure of the one-layer enamel coating on aluminum is not investigated.

Therefore, from the theoretical and practical points of view, it is essential to study the structure of one-coat low-melting aluminoborophosphate coating for aluminum houseware.

The x-ray- phase analysis did not identify crystalline phases in the surface layer of the coating, and only a tendency for crystallization was observed. The diffraction pattern of the contact layer between the metal and the coating only had lines of $Al_2O_3 \cdot Cr_2O_3$ and $Al_2O_3 \cdot P_2O_5$, as well as crystal of the type of $Na_2O \cdot P_2O_5$ (Fig. 1).

An electron-microscope study of a section of the enamel – metal composite established that the transitional aluminum – coating layer has a laminated glass-ceramic structure (Fig. 2).

To ensure strong adhesion in the aluminum – enamel composite, it is necessary to create a strong bond of the transitional layer both to the metal and to the vitreous coating. This is possible due to the intense reactions in the contact zone, resulting in the formation of the transitional layer. The rate of formation of the transitional layer depends on the oxide film on the surface of the aluminum and on the composition and thickness of the enamel coating.

Most probably the adhesion of coating to metal is achieved due to the reaction between chromium ions in the surface layer of the substrate and aluminum, with free access of oxygen to the contact zone. In this case compounds similar to $Al_2O_3 \cdot Cr_2O_3$ are formed. Furthermore, after the melting of enamel begins, aluminum ions and aluminum oxide interact with the $[PO_4]^{4-}$ group contained in the melt and forms $Al_2O_3 \cdot P_2O_5$ compounds; next, $Na_2O \cdot P_2O_5$ are crystallized in cooling and the solidified vitreous phase is closely fixed to these crystals. The strength of the composite is due to the formation of the Cr – O – Al – O – P – O – Na bond, starting with the chromium compounds incorporated in the surface layer of aluminum and ending with sodium ions contained in the vitreous phase.

The chromium ions isomorphically replacing aluminum ions in the surface layer and easily reacting with aluminum oxide in the melt presumably promote the formation of a transitional layer and provide for its direct bond with the metal.

The structure of the metal – coating composite determines the strength of adhesion, chemical resistance, heat resistance, and other properties of the final coating.

Its is known that the properties of the coating and the composite in metal – coating systems to a great extent depend on coordination of their thermal characteristics. The dilatometric properties of glasses (TCLE and deformation start temperature $t_{d.s}$) are the most essential service parameters. In the enameling and other sectors of industry using glass-to-glass, glass-to-metal, glass-to-ceramic seals, etc.,

appropriate selection of the TCLE not only determines the quality of the coating, but is responsible for the very possibility of its production. The TCLE is also very important in all cases where glass or enamel coatings withstand sharp temperature fluctuation or operate with significant temperature differences. Any coating should be carefully matched to a metal substrate with respect to its physical properties, mainly its dilatometric characteristics. In the case of aluminum this is especially significant, since the TCLE of aluminum is very high (about $250 \times 10^{-7}\ K^{-1}$).

Therefore, the TCLE of a coating and its agreement with the TCLE of aluminum, as well as the $t_{d.s}$ of the coating, are among the main quality criteria for aluminum – aluminoborophosphate coating composites.

Analysis of the data obtained shows that the TCLE of coatings varies from 123×10^{-7} to $156 \times 10^{-7}\ K^{-1}$ in the temperature interval of $20 - t_{d.s}$ and the proper $t_{d.s}$ varies from 380 to 440°C. An chromium oxide additive raises the $t_{d.s}$, which is due to the high melting point of this oxide.

The difference between the TCLEs of aluminum and the coatings exceeds the admissible 20% [2] and is equal to about 40% of the TCLE of aluminum, i.e., over $100 \times 10^{-7}\ K^{-1}$. The strength of adhesion of the coating to aluminum increases as the difference between the TCLEs of aluminum and enamel grows.

Enamel coatings obtained on the basis of silicate glass matrices for enameling aluminum have TCLE $(200 - 220) \times 10^{-7}\ K^{-1}$, which differs from the TCLE of aluminum by not more than 20%, which accounts for the parameters of the coating [3]. However, in our case the difference between the TCLE of enamel and metal is very high and therefore is of special interest to investigators.

This is presumably due to the multiphase composition and complex structure of the traditional metal – coating layer. The main components of the glass-enamel coating and the transitional layer are the following crystal phases: $Na_2O \cdot P_2O_5$, $Al_2O_3 \cdot P_2O_5$, and $Al_2O_3 \cdot Cr_2O_3$. Such phases, for instance $Al_2O_3 \cdot Cr_2O_3$, which has a spinel structure, contribute to ensuring high strength of adhesion of the coating to the metal and high thermal resistance.

As a consequence of the above studies, an aluminoborophosphate coating has been developed for household aluminumware, which satisfies the requirements imposed.

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